Cycling of iron and manganese in freshwater, estuarine and deep sea sediments

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1. Introduction

1.1. Iron in marine systems

Iron is an important metal for living organisms, as iron is required for respiratory pigments, proteins and many enzymes. Besides the other nutrients iron availability may limit primary production and thereby the food availability for heterotrophic organisms and the oceanic CO_2 uptake from the atmosphere. Iron limitation of phytoplankton has consequently received a lot of interest. In some oceanic regions there is a low biomass despite a high concentration of nutrients (the high nutrient – low chlorophyll-a (HNLC) regions) and since the start of the 20th century research and speculations have been made about the causes (Gran 1931, Heart 1934 in:de Baar et al. 1990, De Baar et al. 1999, Martin 1990, Martin et al. 1994). Because ambient iron concentrations are low, iron limitation of primary production has been tested by bottle incubations as well as large scale *in situ* experiments for a number of the HNLC-regions e.g. the sub-arctic and equatorial Pacific and the Southern Oceans (Pakulski et al. 1996, DeBaar et al. 1995, de Baar et al. 1990, de Baar et al. 1999b, Behrenfeld and Kolber 1999, Hall and Safi 2001). The phytoplankton communities in these areas are not iron starved *per se*, but the low ambient iron concentrations may constrain biomass accumulation (Martin et al. 1994, Coale et al. 1996, Boyd et al. 2000). However, most results indicate that iron is not the only limiting factor for primary productivity. Other factors are probably as important or are affected by iron enrichments, for example a seasonal wind mixing effect on the light regime or regional silica limitation for diatoms in the remote pacific waters of the southern Ocean (de Baar et al. 1999a). The effect of iron enrichment in the HNLC regions on the bacterial community has not yet been investigated in detail. It appears that the bacterial biomass is not limited by iron (alone) (Church et al. 2000, Hall and Safi 2001). However addition of iron had a considerable impact on the microbial components of the food web (Hall and Safi 2001).

The sources of iron for the pelagic community are several. Aeolian input with teregenous matter is a source occurring in a large part of the oceanic waters (Donaghay 1991, Duce and Tindale 1991, Bowie et al. 2002). Riverine input is another source, especially affecting iron concentrations in coastal areas. In deeper water re-mineralization of organic matter can release iron and after upwelling this can be a source of iron. Finally, sediments can be a source of iron if sedimentary

iron oxides are reduced (directly or indirectly) during anaerobic mineralization processes and then escape to the overlying water. This last process couples the iron cycle to the carbon cycle.

1.2. Organic carbon

Autotrophic organisms fix carbon dioxide during the assimilation processes and form organic carbon molecules. The organic matter produced in pelagic water sinks down together with other settling materials and may arrive at the sediment surface. During sinking the remineralization of organic matter to CO_2 starts. After settling to the sediment surface and mixing into the sediment the organic matter is further degraded by various (micro) organisms. Most of the produced organic carbon is eventually remineralized to CO_2. A small part is of the organic carbon is removed from this short-term biological cycle by burial. Thereby it enters the long-term geological carbon cycle.

1.2.1. Coastal areas

Marine systems account for about halve of the global primary production. Despite the relatively small surface area of the coastal areas, i.e. 8 % of the global ocean surface, these regions contribute 18-35 % to the global production of the ocean. This high productivity is due the river input of nutrients, upwelling of fertile deep waters, the absence of losses below a compensation depth and the close coupling between benthic and pelagic systems (Wollast 1991).

Organic carbon in marine sediment results form several resources: (1) benthic organisms that form organic tissue and faeces, (2) deposited pelagic organic carbon that reaches the sea floor before it is degraded, e.g. produced by autotrophic organisms in the surface waters fixing carbon dioxide and (3) input of external organic carbon e.g. via wind transported dust or run off of adjacent land via rivers. In shallow ecosystems a large fraction (50%) of the organic carbon produced reaches the sea floor where it drives diagenesis (Heip et al. 1995). In contrast to the deep-sea where most organic carbon (> 90 %) is remineralized before the sediment surface is reached. Due to particle mixing and sediment accumulation the settled organic matter is transported to the deeper sediment layers. This ensures a more uniform depth distribution and enhanced diagenetic activity at large depth. The preservation of organic carbon in the sediments depends on many environmental factors (sedimentation rates, grain size of sediments, faunal activity etc.) and the efficiency of the mineralization pathways.

1.3. Organic matter degradation

The efficiency and degradation rate of organic carbon depends among others on the quality of the organic matter pool. The quality of organic matter pool is a function of availability, the composition of the organic matter and the consumer involved. Simple structures like glucose are easily remineralized whereas complex structures like cellulose are more refractory. Breakdown of highly reactive organic carbon results in a high-energy gain for the bacteria. Therefore these components are preferentially degraded, leaving the more complex structures behind. Thus in sediment profiles the composition of the organic carbon pool usually becomes more refractory in the deeper layers (Middelburg 1989). The decrease in organic matter lability and the decrease in concentrations with depth results in a decrease of degradation rates in these deeper layers (Dauwe et al. 1999).

Table 1. Free energy gain from mineralization reactions from Froelich 1973. Energy gain is presented as kJ mol-1 glucose. Organic carbon is represented by CH_2O.

Process	Reaction	Energy gain (kJ $mole^{-1}$)
Oxic degradation	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-3190
Nitrification	$5\ CH_2O + 4NO_3^- \rightarrow CO_2 + 2N_2 + 4HCO_3^- + 3H_2O$	-2750
Mn-reduction	$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	-3090
Fe-reduction	$CH_2O + 7\ CO_2 + 2\ Fe_2O_3 \rightarrow 4\ Fe^{2+} + 8\ HCO_3^-$	-1410
sulphate reduction	$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-380
Methanogenesis	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-350

1.3.1. Oxidation pathways

Mineralization of organic carbon is an oxidation reaction because zero valent carbon in organic matter is oxidized to tetravalent carbon in carbon dioxide. The microbial degradation pathways cover a wide range of aerobic and anaerobic reactions, using different types of electron acceptors. The energy gain of the oxidation-reduction reaction determines the profit for the bacterial community involved and depends on the redox couple. Pathways with a high-energy gain are preferentially used over pathways with a lower gain (Table 1 from Froelich et al. 1978). In sediments the availability of the electron acceptors is limited and preferential use of the most favourable electron acceptor results in zonation of the pathways. This creates a vertical layering, starting with oxygen as the most

favourable electron acceptor, followed by nitrate, Mn-oxide, Fe-oxide, sulphate and finally methane formation (Fig. 1). Due to spatial heterogeneity of dynamic sediments (bioturbation, micro-niches) the vertical separation is not very strict and several processes may occur at the same depth in different patches (Davison et al. 1997, Harper et al. 1999).

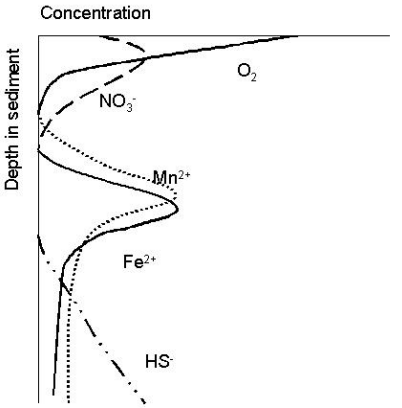

Fig. 1 Redox zonation in marine sediments. First O_2 and NO_3^- are depleted, deeper in the sediment concentration Mn^{2+} and Fe^{2+} increase paralel with the process of metal oxide reduction, followed by an increase in HS^-.

The occurrence or dominance of degradation pathways and electron acceptors depends not only on the energy gain of organic matter oxidation but also on other specific characteristics such as energy gain with respect to re-oxidation of the reduced products, inhibition by products of the other pathways or electron acceptors and chemical reduction processes.

Aerobic organic carbon degradation, using oxygen as electron acceptor, is the pathway with highest energy gain. Diffusion of oxygen into the sediment is usually limited and at high or intermediate organic carbon loads oxygen is depleted within the first 1-2 cm of the profile (Revsbech et al. 1980). At high organic carbon inputs sediment oxygen consumption is not exclusively attributable to organic carbon degradation. The re-oxidation of upward diffusing reduced products also consumes oxygen (Soetaert et al. 1996). The importance of organic carbon degradation via the aerobic pathway differs and is relatively low (~10 % of total organic matter mineralization) in sediment with a high organic carbon input to approximately 100

% of total organic matter mineralization in organic poor sediments like the ones found in the Mediterranean deep-sea areas (this thesis).

Aerobic organic carbon degradation is relatively fast and efficient. There has been and still is much debate about the effect of oxygen on organic matter degradation. Kristensen and Holmer 2001, reviewed the literature and argued that for highly degradable organic matter aerobic and anaerobic degradation rates are similar, whereas the aerobic pathway more efficiently degrades refractory organic matter. Dauwe et al. 2001 proposed that differences between aerobic and anaerobic degradation are mainly related to absolute mineralization rates and do not necessarily depend on the lability of the sedimentary organic matter.

Nitrate is a dissolved electron acceptor that is used after oxygen becomes lower than a few μM. The dissimilatory reduction of nitrate can be coupled to oxidation of organic matter or re-oxidation of Mn (II) or Fe (II) (Straub et al. 1996). Nitrate reduction occurs in a small layer directly after oxygen is depleted. The importance of nitrate for the organic matter degradation depends on the amount of nitrate, temperature, the oxygen concentration and the availability of organic carbon (Middelburg et al. 1996b). Middelburg et al. 1993 estimated the total contribution of nitrate to organic carbon mineralization at 7-11 %. Availability of nitrate as an oxidant is often restricted because it is one of the limiting nutrients for primary production (Ryther and Dunstan 1971). In freshwater sediments, the role of NO_3 in organic matter degradation is usually larger because of the higher concentrations (Knowles et al. 1981).

Manganese oxides are intermediate sub-oxic electron acceptors in particulate form. In marine sediment most manganese oxide is present in the solid phase because of the low solubility of Mn (III) and Mn (IV). Reduced manganese mostly occurs in the porewater as solute, because this form is more soluble. However, reduced manganese can also adsorb onto sediment particles or Mn-oxides thereby disappearing from the porewater solution (Canfield et al. 1993b, Slomp et al. 1997). In general sediment concentrations of manganese-oxide are relatively low compared to two other electron acceptors, iron oxide and sulphate. Reduced manganese (Mn (II)) can re-oxidize with nitrate and oxygen. Manganese-oxides exist in various forms, which have different reactivities. Reactivity of manganese oxides is controlled by surface reactions and therefore by factors like surface area and crystallinity (Burdige et al. 1992) Manganese oxide reduction can occur coupled to the oxidation of organic carbon. At low reduction rates surface area and crystalinity are the controlling factors of microbial reduction (Burdige et al. 1992). The importance of manganese as electron acceptor in the organic carbon mineralization depends on the availability and the reactivity of the oxides present.

In some sediments manganese oxides are present in high concentrations like in the Skagerrak S9 site (Canfield et al. 1993b) or the Panama basin (Aller 1990). Here manganese oxide is an important electron acceptor in the organic carbon degradation (Panama Basin: 100 %, S9: ~ 99% S9). Manganese oxide reduction can also occur coupled to the re-oxidation of Fe (II) (Postma 1985), or pyrite and iron sulphide oxidation (Schippers and Jorgensen 2001). Because of the competitive chemical reduction of Mn-oxides and the low sediment concentration of Mn-oxides bacterial Mn-reduction is often assumed to be zero and neglected in a lot of studies.

Iron oxide is a second intermediate sub-oxic electron acceptor. The iron oxide concentration in sediments is usually much higher (10 times) than that of manganese oxide. Due to low solubility of ferric iron or Fe (III), oxidized iron is mostly in the particulate form. Reduced iron (ferrous iron or Fe (II)) is more soluble and can be found in the porewater solution or adsorbed onto particulate matter (Kostka and Luther 1994). Like for manganese various types of iron oxides exist. These range from amorphous structures to highly crystalline oxide forms. Reduced iron forms can be re-oxidized with oxygen, nitrate and manganese oxides as electron acceptors (Postma 1985). Microbial iron oxide reduction can be coupled to the cycling of organic carbon. The relative importance of the iron oxide reduction pathway is very variable. In freshwater sediments iron oxides are the most important anaerobic electron acceptors (Roden and Wetzel 1996). In saline sediments the contribution of iron oxide reduction tot total mineralization varies from 0.2 % of mineralization in the Mediterranean sediments (this thesis) to 78% in the Skagerrak S4 site (Canfield et al. 1993b). Iron oxide reduction can also be coupled to the re-oxidation of sulphide (Sorensen and Jorgensen 1987). Reducibility of iron oxides is determined by their reactivity which, is controlled by crystal structure (Larsen and Postma 2001). More reactive oxides provide a higher energy gain for iron oxide reducing bacteria. The rate of microbial iron oxide reduction can therefore be controlled by reactivity (Jakobsen and Postma 1999, Postma and Jakobsen 1996) and the available specific reaction sites (Roden and Zachara 1996.)

In marine sediments with a high organic carbon input sulphate reduction is the most important anaerobic degradation pathway. Due to diffusion of sulphate from the overlying water into the sediment and the high concentration of sulphate in seawater, sulphate availability is high and this process can account for a large part of organic matter degradation (Henrichs and Reeburgh 1987). Thus in organic rich coastal sediments sulphate reduction is often the major mineralization pathway (20-90% of total mineralization, Jorgensen 1982, Canfield et al. 1993b, Thamdrup and

Canfield 1996). Sulphide, which is one of the main products of sulphate reduction, can re-oxidize with O_2, NO_3, Mn-oxides and Fe-oxides (Jorgensen 1977, Sorensen and Jorgensen 1987, Moeslund et al. 1994). In freshwater systems sulphate concentrations are low and sulphate reduction is not an important degradation pathway in most anaerobic freshwater sediments.

The final mineralization pathway is methane formation, where organic carbon components are fermented. In marine sediments methanogenesis is only of major importance if sediment organic carbon load is sufficient to fuel all preceding mineralization pathways and deplete all stocks of alternative electron acceptors. In freshwater sediments methanogenesis can be an important degradation pathway (e.g. Roden and Wetzel 1996, Conrad and Klose 1999). Methane is oxidized in presence of oxygen (Bender and Conrad 1992, Canfield 1993, Bodelier and Frenzel 1999). Anaerobic methane oxidation by a consortium of sulphate reducing and methane oxidising bacteria has been reported in marine sediments (Boetius et al. 2000) and is subject of intensive study.

The relative importance of the different degradation pathways are affected by (1) The quantity and degradability of the organic carbon. (2) Availability of the electron acceptors to be used in bacterial degradation pathways. At low fluxes of fresh organic carbon, the rate of materialisation is small and oxygen can account for mineralization of all labile organic carbon. At higher carbon fluxes oxygen is depleted and the anaerobic processes become more important, starting with denitrification as dominant process. At increasing carbon fluxes the degradation process shifts to the other pathways until sulphate reduction is the dominant pathway (Fig. 2, Soetaert et al. 1998, Wijsman et al. 2001a). The absolute carbon input at which the changes occur depends on the availability of the different electron acceptors. The models indicate that the changes in dominant pathway do not always occur gradually but may appear in swaps. These swaps have not been observed yet in field measurements, but may be an explanation for the existence of sulphate or iron-oxide reduction dominated sediments. A number of other factors, like temperature and sediment disturbances, affect the rates and distribution of the pathways.

Understanding the factors and mechanisms affecting organic matter degradation pathways is relevant in furthering our understanding and modelling of ecosystems. Together with changes in degradation pathways other aspects, such as redox state, pH, and concentrations of other constituents, might change as well. This can significantly affect the system. Many trace metals, like cadmium and lead, are sorbed or incorporated within sedimentary manganese or iron oxides. Dissolution of these oxides as a consequence of organic matter degradation may result in

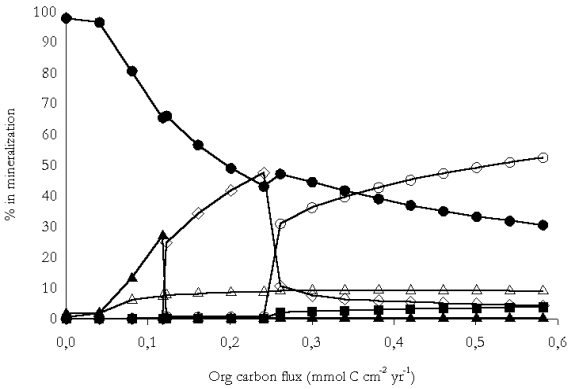

Fig. 2 Effect of the organic matter flux (mmol C m^{-2} yr^{-1}) to the sediment on the relative importance (%) of the various pathways as modelled by Wijsman et al. 2002. Oxic materialisation - solid circles, nitrification - open triangles, Mn-oxide reduction - solid triangles, Fe-oxide reduction – open diamonds, Sulfate reduction - open circles, methanogenesis - solid squares.

liberation of these trace metals as well thereby linking the iron and trace metal cycles (Warren and Haack 2001, Zachara et al. 2001), for example Pb, Zn, Cu and Cd co-precipitate with iron oxides (Tessier et al. 1985, Dong et al. 2000, Lee et al. 2002). Studies have shown that the sediment oxygen state affects trace metal concentrations. Cd, Cu, Mo, Re, U and V are enriched in anoxic sediments (see references in Namerhoff et al. 2002). Fein et al. 1999 described the concomitant release of Al, Co, Cr, Cu Ni, Pb Ti and V from rocks by bacterial activity. Besides, some metals are highly dissolved in their oxidized state, whereas their reduced forms may be insoluble sulphides (Warren and Haack 2001, Skei et al. 1988). Therefore changes in sediment redox conditions affect mobility and bioavailability of these components. Morse 1994 described the bioavailability of trace metals, which co-precipitate with iron pyritization. Phosphor, which is an important nutrient, is associated with iron oxides. Dissolution of iron oxides due to changing redox-conditions or dissimilatory iron reduction results in liberation of phosphate as well, eventually resulting in eutrophication of the system (Nixon 1981, Roden and Edmonds 1997). Sulphate reduction results in the production of HS^- that is toxic for most benthic organisms (Magni and Montani 1998). In environments containing reactive metal oxides these can act as a buffer of the system against HS^- by re-oxidising the sulphide and forming metal sulphides (King 1990, King and

Klug 1982). Hereby suitable conditions are maintained for as long as the metal oxide buffer exists.

In rice paddies and wetlands the importance of the different degradation pathways determines the potential methane efflux towards the atmosphere. Because of the large capacity of methane as a global warming gas, and the large area of rice fields needed to feed a growing global population, the process of methane production, effluxes to the atmosphere and limiting factors of these have been a subject of interest for several years (e.g. Kruger et al. 2001, Frenzel et al. 1999, van Bodegom and Scholten 2001).

Recently, interest has grown on the role of anaerobic and metal-oxide reducing microorganisms in soil remediation. Langenhoff et al. 1997 reported that microbial reduction of manganese could be coupled to toluene degradation. Using less crystalline manganese oxides or adding organic ligands can enhance the degradation rates. Dissimilatory iron-oxide reducing organisms have the ability to destroy organic contaminants, including chlorinated contaminants and aromatic hydrocarbons, by oxidising them to CO_2 (Lovley and Anderson 2000). Like for manganese-oxide degradation the use of chelators enhances iron oxide reduction rates (Lovley et al. 1996). Moreover iron oxide reducing bacteria have been found to reduce other metals and convert them to soluble forms that are likely to be immobilised in the subsurface (Lovley et al. 1991**,** Warren and Haack 2001).

Providing an electron acceptor in the form of an anode enlarges the remediating capacity of iron oxide reducers (Bond et al. 2002). Furthermore, iron-oxide-reducing bacteria in marine sediment are able to conserve energy to support their growth by oxidising organic carbon with an electrode as the sole electron acceptor (Bond et al. 2002). Energy stored in organic matter can be harvested with this pathway by placing an anode in the anoxic sediment zone and a cathode in the oxic zone. This finding provides a potential method to harvest energy from wastewater.

1.4. Metal oxide reduction

The mineralization pathways involving dissolved constituents, O_2, NO_3, SO_4 and CH_4 have been studied intensively and a lot of knowledge has been gained. Microbes using the metal-reduction pathways have been discovered only about two decades ago (Lovley 1987, Lovley and Phillips 1986, Phillips et al. 1993). Because of the low transport rates of these particulate electron acceptors these mineralization pathways have been considered of no or limited importance for a long time and were therefore not included in studies on mineralization pathways. This traditional view changed with the recognition of intensive sediment metal

recycling, allowing one metal molecule to be used in organic matter degradation a number of times before burial (Fig. 3, Aller 1990). Solid phase metal oxide is reduced in the metal oxide reduction zone in the anoxic sediment. The reduced metal, which is dissolved in the porewater, can re-oxidize after diffusion into an aerobic layer or by reaction with a re-oxidizing agent. A subsequent mixing event, like bioturbation, mixes the newly formed particulate metal oxide into the reducing layer where the metal can be re-used. As long as no metals escape this cycle, metal oxide reduction can continue. If the cycle is not complete this may lead to an efflux of reduced metals to the overlying water or burial of metal-oxides in the sediment. The final effect of cycling on mineralization pathways depends on the recycling rate and the presence of the other electrons. Studies on the role of metal oxide reduction in organic carbon mineralization in marine sediments showed a broad range of rates and relative importance (e.g. Aller 1994b, Canfield et al. 1993b, Thamdrup and Canfield 1996, Glud et al. 1998). In anaerobic freshwater sediments iron oxide can be the most abundant electron acceptor and therefore an important component in anaerobic degradation (Roden and Wetzel 1996).

Nowadays, iron and manganese oxide reduction are known to be potentially important pathways for organic matter degradation and both have been discussed in a lot of studies (e.g. Canfield et al. 1993b, Kostka et al. 2002, Thamdrup and Canfield 1996, Slomp et al. 1997, Wijsman et al. 2001a, Roden and Wetzel 2002). However, the solid phase nature and chemical properties of these oxides do impose some difficulties on the experimental research. Metal oxide reduction rates are often estimated by subtracting other pathways (which can be relatively easily determined) from total organic degradation rates, resulting in a lumped rate for metal-oxide reduction.

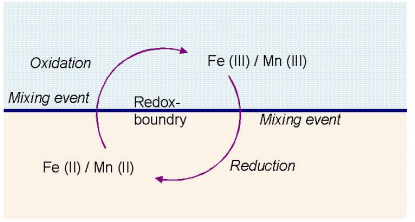

Fig. 3 Metal cycling across a redox boundary. Cycling of metals can occur within the sediment or across the sediment – water interface. The term 'mixing' involves both dissolved and particulate mixing mechanisms, such as bioirrigation and bioturbation respectively.

1.4.1. Reduction rates

Establishing the role of metal oxide reduction in organic carbon degradation at different conditions is an important aspect to model biogeochemical sediment processes, and to gain insight in bio-remediation potentials. However, chemical and kinetic characteristics of the metal oxides are more complex than of the other electron acceptors. Therefore studying metal oxide reduction is rather complex and laborious. Especially side reactions that cause reduction or re-oxidation of the metal (Postma 1985, Canfield et al. 1992, Sorensen and Jorgensen 1987) or precipitation and adsorption on clay particles, cell surfaces or iron oxides (Roden and Zachara 1996, Kostka et al. 1999a) complicate rate measurements. These side reactions should either be measured as well, or prevented by using inhibitors (Oremland and Capone 1988, Canfield et al. 1993b).

1.4.2. Reactivity

Energy gain and preferences of bacteria to use metal oxides depend on the crystal structure of the oxide (Jakobsen and Postma 1999, Postma and Jakobsen 1996) Amorphous metal oxides are very reactive and can easily be used by bacteria at a high rate, whereas more crystalline phases provide lower energy gain, which reduces the competition position of metal oxide reducing bacteria towards sulphate reducers. Sedimentary metal oxide reactivities provide insight on the potential for metal oxide reduction pathways. Traditional methods are based on iron oxide speciation and concentration. However, these are affected by pool size and sediment specific surface area and are not suitable for comparing reactivity between samples with different characteristics. Reactivity of some iron oxides towards dissolution has been studied, indicating that less polymerised or less crystalline oxides dissolve better (Deng and Stumm 1994). This does not allow for a quantification of iron oxide reactivity in sediment containing a mixture of iron oxide species. A decade ago Postma 1993 reported a method to quantify iron oxide reactivity using a reactive continuum approach. Using this method Larsen and Postma 2001 reported the reactivity of pure iron oxides to be independent of pool size and the specific surface area. Recently Van der Zee and van Raaphorst 2002 applied this approach to assess manganese oxide reactivity in North Sea sediments. Applicability of this method for a range of sediments has not been tested yet. Testing a range of sediments is necessary to estimate the usefulness of this method in biogeochemical research. Besides, if reactivity data are to provide insight in the potential microbial reduction of the oxides investigating this link will be necessary as well. As far as we know, the method is not yet linked to data on iron oxide reduction rates.

1.4.3. Bioturbation effect

Aller 1990, Aller 1994b described the effect of bioturbation on the importance of manganese reduction for organic matter degradation. He established the important role for particle mixing as this allows newly formed metal oxides to be mixed from the upper sediment layer into the reducing layer. The overall effect of bioturbation is a faster mixing and faster turnover due to enlargement of the (sub) oxic surface area via the burrow walls and a higher exchange of porewater and overlaying water (Kristensen 2000). The net effect depends on bioturbation intensity and the initial sediment conditions. Bioturbation can be split in two mechanistic components, sediment irrigation and particle mixing. The effects of these two components are likely different for iron and manganese due differences in their basic aquatic chemistry. In a continental slope sediment Van der Zee 2002 revealed particle mixing as the rate limiting factor for the iron cycle, while particle mixing and oxidation kinetics were rate limiting for manganese cycling. The separate effects of particle mixing and irrigation on the metal reduction pathways have not been experimentally investigated. However this type of information is essential to further our understanding and to improve and validate diagenetic models.

1.5. This thesis

To elucidate some of the lacks in our knowledge on sedimentary iron and manganese cycling the programme on Sedimentary Manganese and Iron cycLEs (SMILE) was started (funded by NWO-ALW). In this research programme the aspects of sedimentary iron and manganese were studied along a carbon gradient. The programme was divided in three components. Component I focused on bioturbation and manganese and iron cycling in estuarine sediments and the results are presented in this thesis. Component II focused on the cycling of manganese, iron and phosphorous in sediments from the continental shelf and slope (Royal Netherlands Institute for Sea Research, results in: Van der Zee 2002) and component III comprised the cycling of Fe, Mn related trace elements and sulphur in sediments of the Eastern Mediterranean (University of Utrecht).

1.5.1. Component I

This thesis describes results of the first component of SMILE. The objectives of the study were:

1. To compare iron oxide reactivity within and between marine sediments and establishing the effect of iron oxide reactivity on iron oxide reduction rates.

2. To investigate the rate of iron oxide reduction as a function of organic carbon and reactive iron oxide loading.
3. Examine the effect of bioturbation and its separate mechanistic components on sedimentary iron and manganese oxide reduction.
4. Studying the importance of metal oxide reduction rates for organic matter degradation in different sediments and the effect of side reactions.

Field and experimental studies are performed with three types of sediment covering a gradient of salinity and organic carbon input. A freshwater site, Appels, was situated along the Scheldt River in the intertidal zone and was flooded twice a day. The sediment was very fine and had a high organic carbon content due to a high organic carbon input from benthic algae and particles from the Scheldt river and the adjacent marsh. Two subtidal estuarine sites in Lake Grevelingen (salinity 29) were selected. One, Vliegertje, is a sandy littoral site situated on a plain, the other, Geul, is situated in a gully. Due to focussing of fine material the sediment in the gully was finer than the Vliegertje sediment. However, at both sites sediments were coarser than at the freshwater site Appels. Organic carbon inputs were much lower as well. A deep-sea sediment was sampled in the Eastern Mediterranean. These sediments are hemipelagic muds with a low organic carbon content and small grain sizes.

Chapter 2 describes a method, the reactive continuum approach (Postma 1993) to quantify iron oxide reactivity in sediments. The iron oxide reactivity is described using a gamma distribution. We compare results of this method for samples from the three sites with results of extractions for iron oxide speciation (e.g. concentration of amorphous iron oxides). The effect of iron oxide pools size and sediment specific surface area on reactivity is evaluated and no simple relations were found.

In Chapter 3 the relation between organic matter input, iron oxide concentration and iron oxide reduction rates was investigated using slurry experiments. Iron oxide reduction rates in the freshwater sediment were dependent on iron oxide concentrations, whereas in the estuarine and deep-sea sediment organic carbon availability was the rate-limiting factor. V_{max} (potential maximal iron oxide reduction rate) and Km (affinity of the microbes for the substrate i.e. iron oxides) have been estimated and were consistent with these findings. In organic-rich freshwater sediment V_{max} of iron oxide reduction was independent or organic carbon concentrations, whereas in deep-sea sediments we found increasing V_{max} values with increasing quantities of degradable organic carbon indicating the dependence on organic matter availability.

The effect of bioturbation on metal cycling has been investigated in a mesocosmos experiment (Chapter 4). Bioturbation can be split in two components: sediment irrigation and particle mixing. The sole and combined effect of these processes on metal oxide reduction was investigated. Due to the differences in the basic chemistry of both metals iron-oxide reduction is primarily affected by particle mixing, whereas manganese oxide reduction is affected by both particle mixing and irrigation.

In Chapter 5 the importance of metal oxide reduction in organic carbon degradation has been investigated in anaerobic bag incubations. The results provide a link between our experimental data and field observations. Metal oxide reduction rates were highly different between the sediments. Metal oxide reduction layers can be discerned within the profiles. Furthermore in the estuarine sediment inhibitors were used to discern chemical and microbial metal oxide reduction rates.

The concluding Chapter 6 integrates our findings of the various chapters and provides a discussion of sedimentary iron and manganese cycling.